CO_2 electro-valorization to dimethyl carbonate from methanol using potassium methoxide and the ionic liquid [bmim][Br] in a filter-press electrochemical cell

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Abstract

BACKGROUND: The electrochemical valorization of CO_2 into added-value products appears as a promising strategy for reducing CO_2 emissions and mitigating climate change. Dimethyl carbonate (DMC) is an environmentally friendly valuable chemical, with multiple applications, and has been suggested as a potential gasoline additive. However, DMC has traditionally been produced from hazardous phosgene and CO routes, which encourages the interest in developing new processes. The aim of this work is to study the valorization process for the direct electrosynthesis of DMC from CO_2 and methanol using CH_3OK and the ionic liquid 1-butyl-3-methylimidazolium bromide, avoiding the addition of carcinogenic compounds.

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RESULTS: The evolution of the concentration of DMC was studied in a filter-press electrochemical cell with anodic and cathodic compartments separated by a Nafion 117 membrane, operating for 48 h. A final DMC concentration of 15.07 mmol·L^{-1} was observed. Moreover, analysis of the by-products obtained in the process revealed the formation of tetramethyl orthocarbonate and dimethoxymethane, which were detected and quantified in the liquid phase. A simplified reaction scheme was also proposed according to the results obtained.

CONCLUSION: Unlike all previous works that used an undivided cell, the new experimental results of this study using a divided cell can serve as a reference for further research to overcome current limitations.

Keywords: Carbon dioxide, valorization, dimethyl carbonate, methanol, ionic liquid, filter-press cell

INTRODUCTION

Anthropogenic emissions of carbon dioxide represent a 3.9% CO_2 annual excess to the natural carbon cycle[1]. The emissions from human activities are mainly attributed to fossil fuel combustion. The key issue of the Intergovernmental Panel on Climate Change (IPCC), of reducing the global CO_2 emissions to 50% by the year 2050 is to avoid a global average temperature rise over 2ºC.[2] The major strategies that are being considered to reduce CO_2 emissions include improving energy efficiency, replacing fossil fuels by renewable energy, carbon capture and storage (CCS) and CO_2 valorization.[3] Carbon capture and valorization avoids the costs associated with CO_2 transportation representing up to 40% of the total cost[4] and allows the conversion of CO_2 into added-value products.[5]

Dimethyl carbonate (DMC) is an environmentally friendly valuable chemical with low ecotoxicity and easy biodegradation. It is used as a safe carbonylation and methylation reagent substituting highly toxic phosgene, dimethyl sulfate and methyl halides.[6] It is also an important intermediate in the production of carbamates, isocyanates and higher carbonates.[7] In addition, DMC has been highlighted as a potential gasoline additive due to its higher oxygen content and lower emissions of hydrocarbons, formaldehyde, CO and particles than methyl tert-butyl ether.[8] Furthermore, its high dielectric constant explains why DMC is also widely used as polar solvent and electrolyte solvent for lithium ion batteries.[5,9] Therefore, the production of DMC has attracted much attention.

Traditionally, the industrial route for DMC synthesis is methanol phosgenation.[7,10] The use of the highly toxic and corrosive hazardous phosgene and the by-production of a HCl stream caused the replacement of this process by EniChem in the mid-1980s.[11] This safer synthesis route involves liquid-phase oxidative carbonylation of methanol. In the late-1990s, carbonylation of methyl nitrite was developed by UBE.[12] Although both EniChem and UBE routes avoid the use of phosgene, they still need the chlorinated derivate catalysts copper chloride and palladium chloride respectively and imply the use of CO.[13] Several alternative routes have been developed of which transesterification of urea, transesterification of ethylene carbonate and direct synthesis of DMC from carbon dioxide are the most promising.[13,14] The transesterification of urea is performed in two steps via a methylcarbamate intermediate.[14] The transesterification of ethylene carbonate is also a two-step route: first, ethylene carbonate is synthesized by the reaction of CO_2 with ethylene oxide, and then DMC is produced by the transesterification of methanol with the cyclic carbonate. However, ethylene oxide is suspected of being a human carcinogen. Therefore, instead of routes that involve several steps, the direct synthesis from CO_2 and methanol appears to be a very interesting route to synthesized DMC and, at the same time, valorize CO_2.

Despite being abundant, nonflammable, nontoxic, and inexpensive, carbon dioxide has slow reactivity and high thermodynamic stability[15]. In order to overcome this issue, different catalysts, such as organometallic complexes, metal oxides and metal halides, have been used requiring high temperatures.[9] High pressure or even supercritical conditions to shift the reaction equilibrium have also been studied.[16, 17] Electrochemical techniques could help supply the energy needed to valorize CO_2 under mild conditions, therefore electrochemical valorization of CO_2 to valuable products in the presence of ionic liquids is gathering special interest. Ionic liquids (ILs) are salts well-known for their unique properties such as negligible vapor pressure, thermal and chemical stability, high ionic conductivity and wide electrochemical window.[9] In the past few years, the electrosynthesis of cyclic carbonates from epoxides[18] and diols,[19,20] and the production of organic carbamates from amines[21] have been reported using ILs. The synthesis of dimethyl carbonate in the presence of ILs has also been focus of special attention in the electrochemical field[15,22-28] with Zhang *et al*.[28] and Feng and Liu[22] respectively achieving 74 and 72% yields in the presence of [bmim][BF4] with a copper working electrode. To improve the yield in the same ionic liquid, Feng *et al*.[23] and Wang *et al.*[25] used a nanoporous copper electrode based on platinum (NPC-Pt) and silver (NPC-Ag), slightly increasing the yield to 81 and 80%, respectively. Attempts with other metal electrodes have also been reported, for example Liu *et al*.[24] reached a 76% yield using an indium electrode. However, all these cited works[22-25,28] achieved a high yield at the expense of using methyl iodide as additive, known to be a category 2 carcinogen. Yan *et al*.[26] also attained a 76% avoiding CH_3I addition and using a platinum electrode in the presence of a different ionic liquid ([bmim][Br]). However, they used propylene oxide, which is also a category 2 carcinogen. Recently, Yuan *et al*.[27] circumvented the use of CH_3I, but they prepared the [Bzmim][Cl] ionic liquid from toxic benzyl chloride, achieving 3.8% yield of DMC with graphite electrode. Ionic liquids act as substitutes for conventional toxic and

volatile solvents but the environmentally friendly issue is bypassed when toxic chemicals are added to the process. In this sense, Yuan *et al*.[15] achieved a 3.9% yield of DMC in [bmim][Br] as electrolyte with Pt electrodes adding CH_3OK as the co-catalyst, avoiding the addition of toxic chemicals.

Hence, electrochemical valorization of CO_2 to DMC has had special interest in the literature over the last years. Although all the previous works on the electrosynthesis of DMC from CO_2 used an undivided cell, this type of cell does not allow the study of the development of the process in a continuous mode with separated anodic and cathodic compartments. Divided cells are characterised by their wide versatility and easy scale-up, which give them potential for industrial production.[29] Moreover, divided cell configuration allows the prevention of DMC degradation on the surface of the counter electrode.

The aim of this work is to study a CO_2 valorization process for the electrosynthesis of DMC from methanol using the IL [bmim][Br] and CH_3OK, thus avoiding the addition of carcinogenic compounds. Unlike previous references that studied this electrosynthetic route in an undivided cell, here the performance is investigated in a filter-press electrochemical reactor operating for up to 48 h. The identified products are described, a reaction scheme of the process is proposed and a kinetic analysis of DMC formation is also carried out. This work gives experimental evidence that will be useful as a reference for the evaluation of future improvements.

EXPERIMENTAL

Materials

Methanol (Panreac, PA-ACS-ISO, 99.8%), potassium methoxide (Sigma-Aldrich, 95%), dimethyl carbonate (Sigma-Aldrich, anhydrous, ≥99%), dimethoxymethane (Sigma-Aldrich, 99%), 2-propanol (Sigma-Aldrich, anhydrous, 99.5%), trimethyl orthoformate (Sigma-

Aldrich, 99%), tetramethyl orthocarbonate (Sigma-Aldrich, 98%), hydrochloric acid (Sigma-Aldrich, ACS reagent, ≥37%), 1-butyl-3-methylimidazolium bromide [bmim][Br] (IoLiTec, 99%), 1-ethyl-3-methylimidazolium ethylsulfate [emim][$EtSO_4$] (Sigma Aldrich, >95%) were used as received without further purification, except the ionic liquid [bmim][Br] that was dehydrated in an oven at 313 K and total vacuum for 12h, since it is highly hygroscopic. Carbon dioxide (99.7%) was purchased from Air Liquide.

Experimental set-up

Fig. 1 shows the experimental set-up. A filter-press electrochemical cell (Micro Flow Cell®) supplied by ElectroCell was used in this work. The cell was divided into anodic and cathodic compartments by a Nafion® 117 cation-exchange membrane. Cathode and anode electrodes consist of a Pt/Nb plate (99.5% Pt) with a surface area of 10 cm^2. A leak-free Ag/AgCl 3.4 mol L^{-1} KCl reference electrode was placed very close to the working electrode surface.

Catholyte and anolyte solutions were magnetically stirred and heated at 303 K in sealed glass tanks. A condensing temperature of 279 K was imposed to minimize methanol losses, using a PolyScience circulating bath (AD07R-20-A12E). Both electrolytes were circulated by means of peristaltic pumps (Watson Marlow 323 S/D) with a flow rate of 20 mL min^{-1}. A septum device was incorporated to the output of the electrolyte tanks to enable sampling.

Experiments were carried out under potentiostatic conditions using a potentiostat/galvanostat AutoLab PGSTAT 302 N (Metrohm, Inc.). All experiments were conducted at a 1.2 V potential between the working and reference electrodes. The equipment was controlled by General Purpose Electrochemical System (GPES) software.

Experimental procedure

In a typical procedure, each of the tanks was filled with 200 mL of methanol in which the required amount of [bmim][Br] and CH_3OK had been added according to the specified compositions in Table 1. Then, CO_2 was bubbled into one of the tanks until saturation. Prior to each experiment, the Nafion® membrane was pretreated with HCl (37%) at 313 K for 45 min, to eliminate attached particulates and possible contamination. Afterwards, it was rinsed with ultra-pure water. The membrane was stored in methanol for at least 12 h before use. Electrodes were also pretreated with HNO_3 (11%) to remove surface adherences and then rinsed with ultra-pure water.

The electrochemical experiments were carried out for up to 48 h. Samples were taken at different times to be analyzed in duplicate. Maximum standard deviations for duplicates of the same point in the same experiment were lower than 15%.

The products in the liquid phase were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent Technologies, 6890 N, 5975B), using a 60 m x 250 μm x 1.40 μm DB-624 capillary column (J&W Scientific). The system was equipped with an HP 7694 E Headspace Sampler (Agilent Technologies) and 2-propanol was used as internal standard.

RESULTS AND DISCUSSION

Influence of the composition in the working compartment

Different experiments were carried out to study the influence of the composition of the reaction medium in the working compartment and to obtain evidence of the possible role of the species involved in the system. Table 1 summarizes the composition (weight %) of the

different components considered in each experiment, together with the value of concentration of the desired product DMC after 6 h of operation.

A series of experiments were initially performed with the aim of gathering evidence to ascertain the possible role of CH_3OK and the IL [bmim][Br] in the electrosynthesis. A first experiment (E1) was performed in the absence of [bmim][Br]. As Table 1 shows, no significant concentration of DMC was observed when only CH_3OK is used. This reveals that the formation of DMC cannot be achieved without [bmim][Br] in the system. However, using only [bmim][Br] in methanol is not sufficient, as when CH_3OK was not included and only [bmim][Br] was used (experiment E2), the concentration of DMC was still close to zero. However, experiments carried out with both [bmim][Br] and CH_3OK (E4-E7, table 1) gave concentrations of DMC that were 1 or 2 orders of magnitude higher. Therefore, it can be concluded that the simultaneous presence of both CH_3OK and [bmim][Br] is required to obtain the desired product DMC.

Although the results show the need for the IL [bmim][Br], its role is not clear as it could be assumed to be an electrolyte, rather than taking part in the electrosynthesis. In order to test this hypothesis, in experiment E3, [bmim][Br] was replaced by the electrolyte KBr at the same molar concentration. If the IL was just an electrolyte, it might be expected that replacing [bmim][Br] by KBr (i.e. a common salt with the same anion as the ionic liquid) would not affect the performance. However, under these conditions the quantity of DMC observed was still close to zero. Consequently, the results suggest that [bmim][Br] is not merely an electrolyte, but it plays a catalytic role in the electrosynthesis of DMC.

Three more compositions were then analyzed using both CH_3OK and [bmim][Br] in methanol at different concentrations. Table 1 shows that the highest concentration of DMC was obtained in E5. It should be noted that in E6 doubling the concentrations of CH_3OK and

[bmim][Br] with respect to the best experiment E5 did not improve the performance and resulted in lower DMC yield.

Finally, the concentration of methanol was halved, maintaining the concentration of CH_3OK and [bmim][Br] (E7). For this purpose, the ionic liquid [emim][$EtSO_4$] well-known for its high CO_2 solubility, was used as solvent. In this way, the CO_2 available for the reaction was not limited to the CO_2 solubility in methanol. However, the use of 40% [emim][$EtSO_4$] + 40% methanol (E7) yielded a lower concentration of DMC than using just 80% methanol (E5).

Consequently, it can be concluded that the best results were achieved with 5% CH_3OK, 15% [bmim][Br] and 80% methanol, and therefore, this was the composition that was used for the more detailed studies that are presented in the following subsections.

Products identified by GC-MS and reaction scheme proposed

In addition to DMC, GC-MS analysis of the liquid samples taken during the experiments, showed the presence of the following compounds: dimethyl ether (DME), dimethoxymethane (DMM) and tetramethyl orthocarbonate (OC). Contrary to what is expected from previous work,[15] which reported the formation of both OC and trimethyl orthoformate as liquid products, trimethyl orthoformate was not detected in our experiments. Although DME was not found in Yuan *et al.*,[15] it is a typical byproduct from methanol dehydration obtained in DMC synthesis.[30,31]

Fig. 2 shows the evolution of the average concentration of DMC, DMM and OC in the experimental samples. Since the gas phase was not analyzed, absorbed DME was not measured. As can be seen in Fig. 2, during the first 6h operation the DMC concentration

increased almost linearly strongly. Then a slower rise in the concentration was observed up to 18 h, after which the DMC concentration no longer increased but fluctuated around 15 mmol L^{-1} (1.4 $g \cdot L^{-1}$).

Fig. 2 also shows that the concentration of the by-products OC and DMM was almost zero during the first 6 hours. Then from 6 to 36 h, the formation of OC increased slightly up to 1.74 $mmol \cdot L^{-1}$, while the concentration of DMM remained close to zero. From 36 h to the end of the reaction time, the concentration of OC started to decrease, reaching zero in the last hours of the experiments. However, it should be noted that although the concentration of DMM was close to zero until 39 h operation, from then to the end of the experiments, DMM rose sharply reaching a final value of 17.47 $mmol \cdot L^{-1}$. Therefore, it can be concluded from Fig. 2 that the by-products, especially DMM, were detected towards the end of the experiments, but at shorter reaction times mainly the desired product DMC was produced.

According to these experimental results, a simplified scheme involving parallel and series reactions can be suggested, as represented in Fig. 3. Two main different routes could be distinguished. On the one hand, methanol and CO_2 react to form the desired DMC, and water. On the other hand, the competitive reaction of methanol dehydration to form DME can also take place.[32] Subsequent in series reactions of degradation of the previously formed species would explain the formation of the detected by-products, thus, DMC could be degraded to OC[15] or DME.[8] Finally, DMM appears to be associated to methanol oxidation in the synthesis of DMC.[33,34] Liu and Iglesia[35] proposed the reaction pathways to form DMM via oxidation of methanol or DME, both through a formaldehyde intermediate.

Kinetic analysis of DMC formation

Considering the experimental results obtained in this study, the kinetic analysis of DMC formation was carried out following the differential method.[36] Therefore, the experimental data of the evolution of the DMC concentration with time were fitted and the corresponding rates of DMC formation were calculated. The rate of reaction for DMC formation (r_{DMC}) can be defined as:

$$r_{DMC} = \frac{1}{A}\frac{dn_{DMC}}{dt} = \frac{V}{A}\frac{dC_{DMC}}{dt} \quad (1)$$

Where n_{DMC} is the number of DMC moles formed, V is the volume of electrolyte (V = 0.2 L) and A is the electrode area (A = 10 cm^2). The kinetic expression is referred to the electrode area as extensive magnitude, since the reaction is supposed to take place on its surface or in the very close adjacent fluid layer.[15,23,24,27]

The formation rate of DMC was then represented vs. the DMC concentration obtained (Fig. 4). As can be seen, the maximum value of formation rate (690.4 $mmol \cdot m^{-2} \cdot h^{-1}$) is achieved at the initial time, and then the rate decreased linearly as DMC concentration increased.

Therefore, a linear relationship between r_{DMC} and C_{DMC} is observed. Consequently, it can be suggested that the rate equation to describe the experimental behavior could be expressed as eq. 2:

$$r_{DMC} = k_0 - k_1 \cdot C_{DMC} \quad (2)$$

where the corresponding coefficients (k_0 = 587.2 ± 57 $mmol \cdot m^{-2} \cdot h^{-1}$; k_1 = 38.96 ± 4.66) were calculated with 95% confidence bounds and a goodness of fit of R^2 = 0.952.

In this proposed model, the existence of a first term can be suggested, which describes the formation of DMC. As the methanol reagent is in excess, its dependence could be assumed as a zero order, which results in a constant value k_0.

The second term represents the DMC degradation rate due to the secondary reactions, according to the reaction scheme described previously (Fig. 3). This degradation rate is directly proportional to the concentration of DMC obtained. Thus, in the first hours of the reaction as almost no DMC is formed, this secondary term would be insignificant. Thus, the highest DMC formation rates are observed. As the reaction time progresses, more DMC is formed, which involves a decrease in the r_{DMC} to zero, when equilibrium is achieved and the maximum concentration of DMC is obtained. This $_{CDMC,max}$ could be calculated as eq. 3 describes:

$$\frac{k_0}{k_1} = C_{DMC,max} \quad (3)$$

where $C_{DMC,max}$ has a value of 15.07 mmol·L^{-1}, based on the corresponding coefficients estimated from eq. 2.

The final concentration of DMC achieved cannot be directly compared with other previous studies, as no references for CO_2 electro-valorization to dimethyl carbonate from methanol using a divided cell have been found in the literature. As described in the introduction, the synthesis of DMC using [bmim][Br] and CH_3OK carried out in an undivided cell in excess CO_2, gave a 3.9% yield[15]. In our work, performed in a divided cell and working with excess methanol, a final yield of 12.5% (based on CO_2) was obtained.

CONCLUSION

The behavior of a CO_2 valorization process for the electrosynthesis of DMC from methanol using [bmim][Br] and CH_3OK under mild conditions in a filter-press electrochemical reactor has been studied. Based on the experimental results obtained after operating for up to 48 h, a kinetic analysis of DMC has been developed.

Moreover, unlike most previous work in this field, the quantification of by-products in the liquid phase was performed, which also allowed the study of the evolution of the concentrations with reaction time. In this sense, the formation of DMM in the last part of the experiments was especially noteworthy.

A simplified reaction scheme has been proposed according to the experimental results obtained. Furthermore, it could be concluded from these experiments that [bmim][Br] is not merely an electrolyte, and that the presence of both CH_3OK and [bmim][Br] in the system is required to obtain the desired product. However, further more in-depth research studies will be necessary to confirm the reaction scheme and, especially, to ascertain the reaction mechanism and the possible specific role of the species (e.g. the IL [bmim][Br]) involved in these reactions.

Finally, another contribution of this work is the use of a filter-press electrochemical cell, which could allow the future development of a continuous process with divided anodic and cathodic compartments. The addition of toxic compounds has been avoided, although at the expense of achieving a final concentration of 15.07 $mmol \cdot L^{-1}$ of DMC (1.36 $g \cdot L^{-1}$). In order to optimize the multiple variables involved, future work could focus on the research of new materials for the electrodes, the use of different ionic liquids and the optimization of the operating conditions.

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TABLE

Table 1. Set of experiments performed to study the influence of the composition in the working compartment.

Experiment code	Composition (wt %)					C_{DMC} 6h ($mmol \cdot L^{-1}$)
	CH_3OK (%)	[bmim][Br] (%)	KBr (%)	[emim][$EtSO_4$] (%)	MeOH (%)	
E1	5	0	0	0	95	0.04
E2	0	15	0	0	85	0.27
E3	6	0	9	0	85	0.04
E4	2.5	7.5	0	0	90	3.55
E5	5	15	0	0	80	11.37
E6	10	30	0	0	60	6.64
E7	5	15	0	40	40	6.22

FIGURES

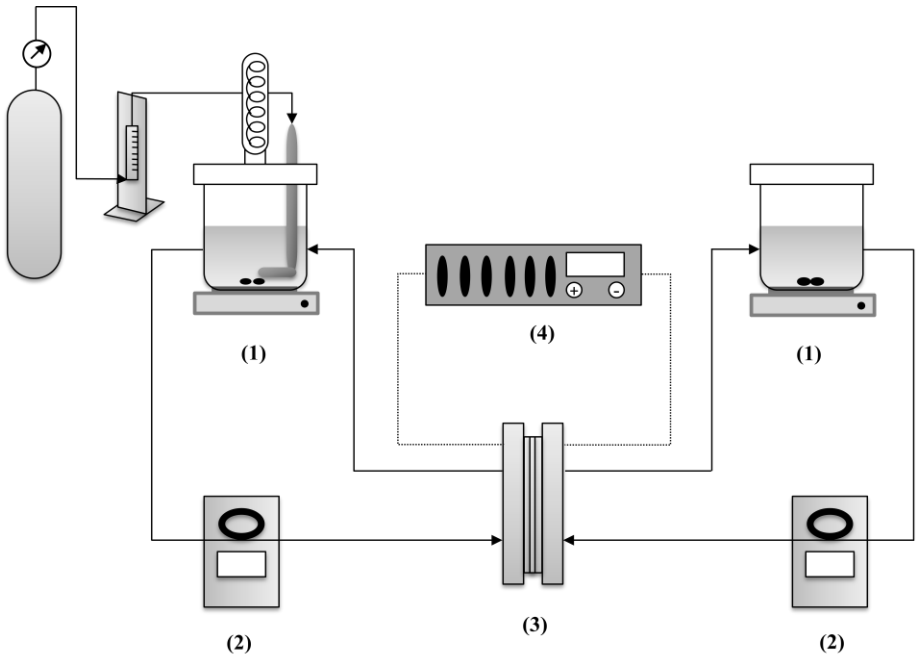

Figure 1. Diagram of the experimental set-up: (1) Storage tanks. (2) Peristaltic pumps. (3) Filter-press electrochemical cell. (4) Potentiostat/galvanostat

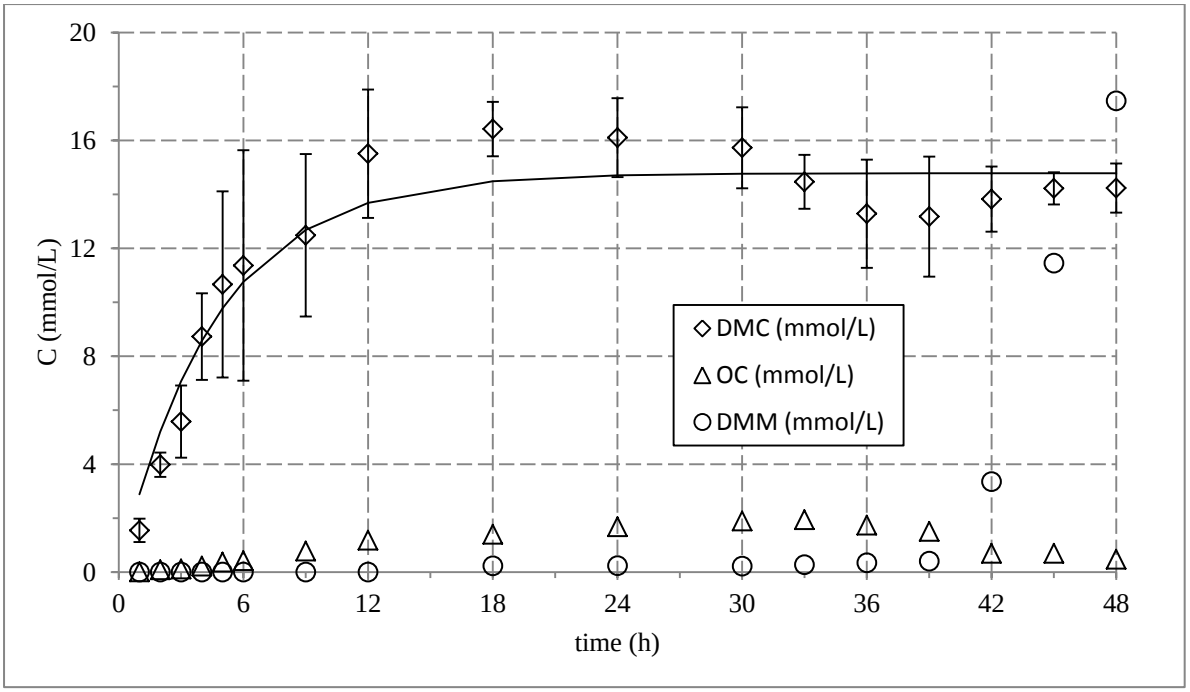

Figure 2. Effect of the reaction time in the concentration of DMC (◇), OC (△) and DMM (○) in the liquid phase

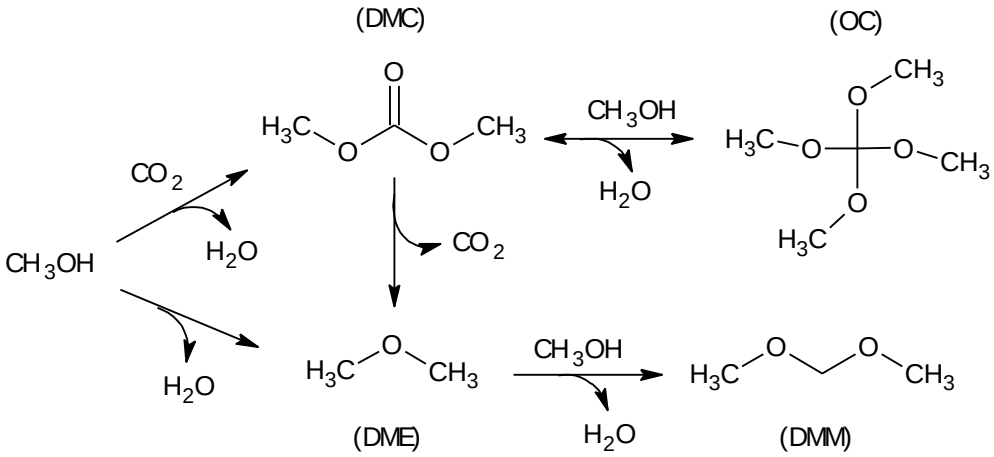

Figure 3. Reaction scheme proposed.

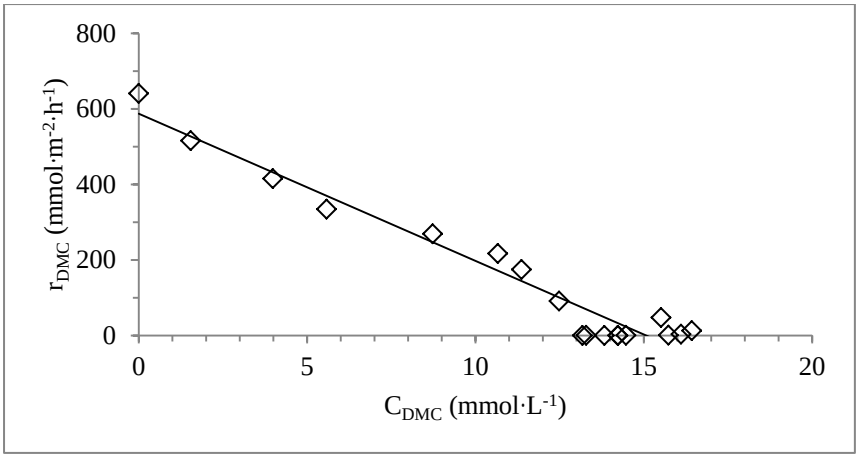

Figure 4. Experimental reaction rates, (r_{DMC}), vs. C_{DMC} (◇) reaction rate of DMC. (-) Fitting of all the data.